### Remarks

Claims 1-22 are pending in the instant application. Claims 1-22 stand rejected under 35 U.S.C. §112, second paragraph, for failing to particularly point out and distinctly claim the subject matter which the applicant regards as the invention. Claims 21 and 22 stand rejected under 35 U.S.C. §101 as improperly defining a process. Claims 1-12 and 15-22 stand rejected under 35 U.S.C. §102(b) as being anticipated by Apfel (WO 97/25097). Claims 1-12 and 18-22 stand rejected under 35 U.S.C. §102(b) as being anticipated by either Berg (WO 94/21301) or Lohrmann (United States Patent No. 5,716,597). Claims 1-22 stand rejected under 35 U.S.C. §103(a) as being anticipated by any one of Apfel, Berg, or Lohrmann in view of Unger (WO 98/10799). Claims 21 and 22 have been cancelled, without prejudice. The rejections are respectfully traversed. Reconsideration is respectfully requested.

### Claim rejections - 35 USC §112:

Claims 1-22 stand rejected under 35 U.S.C. §112, second paragraph, for failing to particularly point out and distinctly claim the subject matter which the Applicants regard as the invention. This rejection is respectfully traversed.

The Examiner objects to claim 1 reciting "heterogeneous gas-containing nucleation sites". The Examiner considers the term "heterogeneous gas-containing nucleation sites" to be indefinite for failing to particularly point out and distinctly claim the subject matter. Applicants respectfully disagree with this characterization of the term. In the field of controlled particle, droplet and bubble formation the terms "heterogeneous nucleation" and "homogeneous nucleation" are well established and well recognised terms. Evidence that these terms were well known to the person skilled in the art at the priority date of the present application (22 April 1998) is provided by the following book extract (copy enclosed):

"Controlled Particle, Droplet and Bubble Formation", David J. Wedlock (Editor), Butterworth-Heinemann (1994), Section 6.2, pages 161-177.

The Examiner's attention is directed to p161 where the statement is made: "Bubbles may arise spontaneously from six quite separate and essentially independent sources, and in each case after their formation, growth to a microscopic size may take place:

- (a) homogeneous nucleation,
- (b) heterogeneous nucleation ..."

Applicants stress that these modes are described as "quite separate and essentially independent". The terms are more fully defined in the subsequent text. Thus, the second paragraph on p. 162 states:

"When bubbles are formed in the bulk of the liquid, well away from any surface (for example, the walls of the container, dust particles or other foreign bodies, or the free liquid surface), the nucleation is said to be 'homogeneous'."

### On page 167:

"Bubbles formed at a surface (e.g. the walls of the container, specks of dust or other inhomogeneities), rather than in the bulk of the solution, are said to be nucleated 'heterogeneously'."

Applicants contend that the terms 'homogeneous nucleation' and 'heterogeneous nucleation' are therefore well established, defined terms in the field of bubble formation. The enclosed reference further emphasises this fact *via* the statement at p.163:

"The theory of both homogeneous and heterogeneous nucleation has been covered extensively in the literature. Particularly comprehensive reviews have been given by Hirth and Pound (1963), and by Zettlemoyer (1969), while an earlier work by Dunning (1955) is still unsurpassed for clarity".

This shows that these terms have been used extensively in the field, and their definition has been known for many decades.

A nucleation site is the place on the surface where the bubble nucleation takes place. Nucleation sites can be added deliberately to a system to enhance bubble formation. The most natural way is to add small particles since these will have a large surface area. In that case, the whole particle may be called a nucleation site.

The Examiner refers to the term "gas-containing heterogeneous nucleation sites".

Applicants stress that the present invention provides oil-in-water emulsion ultrasound contrast agents having separate (i.e. heterogeneous) nucleation sites associated with the emulsion droplets. Thus, the ultrasound contrast agents of the present invention are oil-in-water emulsions which have been modified in such a way that gas-containing nucleation sites are associated with droplets of the dispersed oil phase. An illustration of this would be when the surface of the added particle further comprises a gas, e.g. in a pore or by other means encapsulated into the surface. The present invention teaches that heterogenous nucleation may be further promoted at that particular nucleation site.

The specification describes various methods in which these gas-containing nucleation sites can be provided - see: Page 8 line 29 to page 9 line 31; Page 11 line 13 to page 12 line 13; Example 2 and comparative Example 3; and Example 5 and comparative Example 6.

In view of the above, Applicants respectfully submit that the use of the term 'heterogeneous gas-containing nucleation sites" in Claim 1 is clear to the person skilled in the art. Additionally, the Examiner's comments with respect to claims 21 and 22 are obviated by the cancellation of those claims. Reconsideration and withdrawal of the rejection are respectfully requested.

### Claim rejections 35 USC § 101:

Claims 21 and 22 stand rejected under 35 U.S.C. §101 as improperly defining a process. Applicants respectfully submit that this rejection is obviated by the cancellation, without prejudice, of claims 21 and 22. Reconsideration and withdrawal of the rejection are respectfully requested.

### Claim Rejections - 35 USC § 102:

Claims 1-12 and 15-22 stand rejected under 35 U.S.C. §102(b) as being anticipated by Apfel (WO 97/25097). The rejection is respectfully traversed.

Applicants submit that the oil-in-water dispersions of WO 97/25097 (hereinafter, the '097 reference) are simply that, i.e. no further materials which could provide nucleation sites, in particular gas-containing nucleation sites, are added. Hence, the dispersions of '097 neither contain nor comprise heterogeneous nucleation sites. As is described in the present application, in order to provide the heterogeneous nucleation sites, it is necessary to add an additional component. Preferred examples of these are claimed and recited in Claim 3. In Example 4b, hollow (i.e. gas-containing) polymer-stabilised nanocapsules from step (a) are added to a mixture of perfluorodimethylcyclobutane and perfluorooctanoic acid, followed by shaking. As described at page 18 lines 11 to 14, this gives a dispersion of gas-filled nanocapsules dispersed in a perfluorocarbon. This fluorocarbon dispersion is then shaken with water (lines 14 to 16) to give the desired fluorocarbon emulsion containing gas-filled nanocapsules within the fluorocarbon droplets. The emulsion thus contains fluorocarbon droplets and within the droplets are the gas-filled nanocapsules.

In contrast, '097 teaches emulsions of "drop material" in an aqueous liquid (see page 12 lines 6-19 of '097). There is no teaching or suggestion in this document of the use of additional materials providing gas-containing nucleation sites.

Applicants also point out that '097 <u>does</u> envisage that the vaporisation process for the emulsions therein will be homogenous nucleation, not heterogeneous, - please see page 7 lines 2 to 9; and page 13 lines 2 to 13, of '097.

Applicants stress that heterogeneous and homogeneous nucleation are known to be "quite separate and essentially independent" (see reference cited above), and hence use of this language in claim 1 confers novelty over prior art disclosing only homogeneous nucleation. Also, as discussed above applicants contend that ultrasound contrast agents comprising injectable oil-in-water emulsions wherein there are <a href="heterogeneous gas-containing nucleation sites">heterogeneous gas-containing nucleation sites</a> are not taught or suggested in '097. Consequently, Applicants respectfully submit this document fails to disclose, teach, or suggest the elements of claim 1. Reconsideration and withdrawal of the rejection are respectfully requested.

Claims 1-12 and 18-22 stand rejected under 35 U.S.C. §102(b) as being anticipated by either Berg (WO 94/21301). The rejection is respectfully traversed.

WO 94/21301 discloses <u>solid</u> microparticles which may act as nucleation sites. There is no suggestion that such microparticle should be gas-containing. In contrast, the present invention claims <u>gas-containing</u> microparticles. Where solid microparticulate nucleation sites are used in accordance with the present invention, these are chosen to have properties such as porosity or surface irregularities such that they contain gas. This is described at page 8 line 37 to page 9 line 9 of the present specification (especially p.9 lines 4 to 7). Nowhere does Berg disclose, teach, or suggest gas-containing microparticles.

Therefore, as Berg fails to disclose gas-containing microparticles, Applicants respectfully submit that the present invention is patentably distinct therefrom.

Reconsideration and withdrawal of the rejection are respectfully requested.

Claims 1-12 and 18-22 stand rejected under 35 U.S.C. §102(b) as being anticipated by Lohrmann (United States Patent No. 5,716,597).

US 5,716,597 (hereinafter, the '597 patent) relates to an oil-in-water emulstion comprising a water-insoluble gas-forming chemical and a stabilizer. Applicants submit that the oil-in-water dispersions of the '597 patent are simply such dispersions, i.e. no further materials which could provide nucleation sites, in particular gas-containing nucleation sites, are added. Hence, the dispersions of the '597 patent do not contain or comprise heterogeneous nucleation sites. Moreover, the '597 patent fails to suggest dispersions having heterogeneous nucleation sites.

Therefore, as the '597 patent fails to disclose each and every element of the claimed invention, Applicants respectfully submit that the present invention is patentably distinct thereover. Reconsideration and withdrawal of the rejection are respectfully requested.

### Claim rejections – 35 USC § 103:

Claims 1-22 stand rejected under 35 U.S.C. §103(a) as being anticipated by any one of Apfel, Berg, or Lohrmann in view of Unger (WO 98/10799). This rejection is respectfully traversed.

The Examiner contends that the present invention is unpatentable over any of Apfel ('097), or Berg ('301), or Lohrman ('597) in view of Unger (WO 98/10799). The Examiner notes that Apfel, Berg, and Lohrmann fail to disclose compositions including a vasodilator and Berg and Lohrmann fail to disclose the addition of a drug. The Examiner cites Unger for the use of vasodilators in ultrasound imaging and for the addition of a

drug. Unger is therefore only cited for teachings which are the basis of dependent claims 13-17.

Applicants respecfully submit that Unger fails to correct the deficiencies of Apfel,

Berg, and Lohrmann presented hereinabove, nor even does the Examiner conclude that it

does so. Furthermore, in contravention of the Examiner's assertion, the application of

Unger to any of the cited references fails to disclose, teach, or suggest claims 13-17. As

claims 13-17 are dependent claims, the allowability of the base claims over Apfel, Berg,

and Lohrmann render the dependent claims allowable as well. In view of Unger failing

to correct the noted deficiencies of the cited references, Applicants respectfully submit

that claims 1-20 are patentably distinct thereover. Reconsideration and withdrawal of the

rejection are respectfully submitted.

In view of the remarks set forth hereinabove, Applicants respectfully submit that

the present application, including claims 1-20, is in condition for allowance. Favorable

action thereon is respectfully requested.

Any questions with respect to the foregoing may be directed to Applicants'

undersigned counsel at the telephone number below.

Respectfully submitted,

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## Controlled Particle, Droplet and The state of the s

David J. Wedlock

**Bubble Formation** 

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(१) हिंदू (बिह्नुब्रह्म) की his chapter is divided into four sections, dealing with (i) the formation of the sections of bubbles, (ii) the growth of bubbles, (iii) the detachment of bubbles, and (iv) the role of surfactants in bubble formation and stability

## .2 Formation of bubbles

accompanied by a corresponding increase in the free energy the free energy of the system is reduced by the appearance of bubbles, thus being spontaneous in the thermodynamic sense; and those where bubble formation is We can broadly separate bubble formation into two categories: those cases where

# 6.2.1 Spontaneous bubble formation

concentration of a dissolved gas, as well as by the two previously mentioned a second component may arise, and hence under appropriate conditions bubbles to produce bubbles, as noted by Mori et al. (1976). boiling of the major component, even if it is itself insufficiently supersaturated mechanisms. Note, however, that a dissolved gas may have an effect upon the may be formed as a result of the presence of a greater than equilibrium (ebullition), whereas in a two (or greater) component system supersaturation of form spontaneously in a single-component system only by cavitation or boiling Bubbles may be formed spontaneously in several ways, but note that bubbles can

otherwise unified approach contact angle) this will be discussed in the context of specific alterations to an bubbles of a second component, are similar. Where the second component does have an important influence (see Section 6.4 for the effect on surface tension and Conceptually, boiling in a single-component system, and the formation of gas

macroscopic size may take place: independent sources, and in each Bubbles may arise spontaneously from six quite separate and essentially case after their formation, growth to a

- <u>J</u>E homogeneous nucleation
- heterogeneous nucleation
- **9000** cavitation
  - electrolysis
  - Harvey nuclei
- pre-existing and colloidally stable free bubbles

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present chapter, this drive may arise in two chief ways. themiodynamic drive for the phase change is the excess of chemical potential of the liquid phase as compared with that of the vapour and, for the purposes of the e free liquid surface), then the nucleation is said to be 'homogeneous'. The

### Alteration of temperature

correction and the inequality to atmospheric pressure arise from the fact that initially critical-sized bubbles, which will then rapidly grow. The pressure (usually close to but not exactly equal to atmospheric) sufficiently above In a single-component system, raising the temperature of the system at a constant in deuse liquids, or at great depths, these could be significant. In this context, it there is a hydrostatic head to be considered. Usually, this correction is small, but the appropriately pressure-corrected boiling point will result in the formation of should start near the top of the containing vessel where the hydrostatic pressure is least. The liquid surface itself may be the preferred site for nucleation, where practice, convection will render the liquid thermully inhomogeneous), boiling the role of inhomogeneities will be important. Chief amongst these is likely to be promote or antagonize nucleation (see Section 6.5). A purist might further argue the presence at the interface of surface active species, which might either nucleation (see below). case, and should for this reason be considered in the section on heterogeneous that such nucleation at the free liquid surface is not actually homogeneous in any worth noting that, given a spatially uniform temperature for the liquid (in pressure

pressure. It is of course a commonplace that reducing the pressure above a liquid extensive engineering literature (see e.g. Knupp et al., 1970). For example, the pressure in a liquid can cause cavitation, and this problem has a mature and will cause a reduction in the boiling point. Similarly, reduction of the hydrostatic The vapour may be stabilized with respect to the liquid by a reduction of Alteration of pressure power that can be transmitted by a screw (propeller) to the surrounding water cause breaking of a thread of liquid contained in a capillary tube have a venerable efficiency of screw-driven vessels. Studies of the (negative) pressure required to cavitation (and collateral damage to the material of the screw) limits the hefore the reduction in hydrostatic pressure over the trailing edges causes history, and have been used extensively to test theories of cavity nucleation. Most experiments have actually revealed that the nucleation of caviries is not but takes place preferentially at surface imperfections, probably

> been given by Hirth and Pound (1963) and by Zeitlemoyer (1969), while an called 'classical theories' (Kashtiev and Exerova, 1980; Kashtiev, 1982, 1984, earlier work by Dunning (1955) is still unsurpassed for clarity. More recently, Kashtiev has published several excellent articles covering both atomistic and so-It is noteworthy that bubble nucleation does not have an extensive review given here, sufficient for understanding the later complications. the large number of general nucleation reviews, only a superficial treatment literature, and only rates a mention in the review of Hirth and Pound. In view of 1985; Exerova et al., 1983; Gutsov et al., 1985; Truyunov and Kashtiev, 1986).

expressing this is that the rate of heteronucleation for a given supersuturation low supersaturations, homogeneous nucleation is unlikely. The other way of the heterogeneous case, and the theoretical prediction is that under conditions of statement carries a risk of misinterpretation, however, since the heteronucleation likely to be much greater than the corresponding homonucleation rate. Such a rate will always be limited as sufficiently into the ultimate rate would not be sites. In the case of homogeneous nucleation, the ultimate rate would not be sites. In the case of homogeneous acceptance he limited by the diffusion of rate will always be limited at sufficiently high rates, by the number of heterulimited in this way, though it would of course be limited by the diffusion In general, homogeneous nucleation occurs at higher supersuturations than for

monomer units to the growing nucleus. experimental finding is, of course, that many bubbles are indeed formed in such supersaturation of about 4 for commercially carbonated drinks, for example. The saturation in excess of about 1000: this should be compared with a typical conditions for homogeneous nucleation of CO2 bubbles requires a supersystems. Conditions for homogeneous nucleation are fairly infrequently met, and thus despite its theoretical importance, this type of nucleation is often not us To emphasize this, consideration of the CO2/water system shows that the

practically significant as the heterogeneous case. of two terms - the 'surface' term and the 'bulk' term. The surface term expresses energy of formation of a drop of the (new) liquid phase of radius r is composed stable (and therefore has a higher chemical potential) than the liquid. The free to examine the concept of critical size in the case of a liquid drop formed from various conditions, we introduce the concept of a 'critical' size. It is helpful first the fact that energy must be expended to form the drop/vapour interface of supersaturated vapour. A supersaturated vapour is thermodynamically less Before discussing the kinetic expressions for  $J_i$  the rate of nucleution under

 ${f \Im} G_{\sf surface}$ = 4717-7 interfacial tension \( \gamma \)

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the liquid phase AGT per unit volume of new phase bulk term is due to the gain in free energy as a result of

MR = 4π/2ΔG/3

Overall, the free energy change is given

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Now, the Kelvin equation (eqn (6.4)) relates the curvature of the interface (1/r)  $P_0$ , where  $\alpha = P/P_0$ : to the ratio of the vapour pressure P of a drop of radius r to that over a flat surface

$$2\gamma h = kT \ln \alpha$$

(6.4)

and  $\Delta G_{\mathbf{v}}$  can be expressed in terms of  $\alpha$ , since for a molecular volume of O

$$\Delta G_{\nu} = kT \ln \alpha l \Theta \tag{6.5}$$

appearance of the new liquid phase from the supersaturated vapour ambient supersaturated vapour. The equilibrium at the size  $r^*$  is thus unstable molecule, it becomes essentially free growing, since its curvature is now and the formation of critical-sized droplets is the kinetic bottleneck to the decreased, and its vapour pressure correspondingly reduced below that of the droplet will thus return to individual molecules. If, on the other hand, it gains a and from eqn (6.4) this results in an increased vapour pressure; finally, the  $r^*$ , given by differentiating  $\Delta G_{\text{local}}$  with respect to the radius, and setting the resulting expression equal to zero. This gives the maximum free energy barrier, increasing propensity to evaporate, since its curvature is now greater than 1/1\* drop size. If such a drop loses one molecule (monomer unit), it will have an droplet  $r^st$  corresponding to this maximum in the free energy is called the critical  $\Delta G^*$ , which has to be surmounted in the nucleation process. The size of the As can be seen from Figure (6.1),  $\Delta G_{\text{total}}$  passes through a maximum at a size

a full analysis of the problem is given by Blander and Katz (1975). In terms of P and  $p^*$ , the pressures in the liquid and the vapour pressure of the liquid (at the ambient pressure P), respectively, and the surface tension y: A very similar argument leads to the definition of the critical bubble size, and

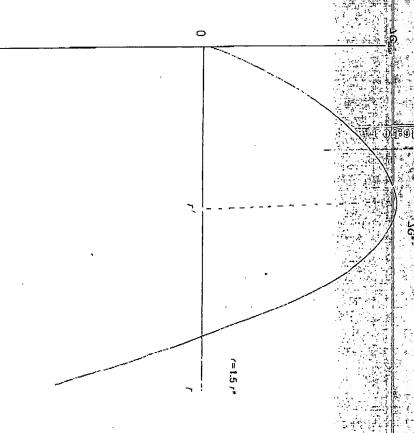
$$r^* = 2\gamma l(p^* - P) \tag{6.6}$$

approximately: In terms of measurable quantities, since  $\alpha \approx p^*/P$ , and 9 I l, this gives

$$r^{\mu} = 2\gamma l \sigma P$$
 (6)

At this size, the bubble is in mechanical equilibrium with the liquid, and the chemical potential of the vapour in the bubble is equal to that of its surrounding

considering the case of boiling (ebullition) in a single-component system. The of critical-sized bubbles formed per unit time, and (ii) the rate at which they most important parameter is (as before) the saturation ratio  $\alpha$ , which for boiling acquire one extra molecule, and thus become free growing. In order to predict the rate of nucleation, we need to calculate (i) the number We start by



evaporate; the equilibrium is unstable. The quantity  $\Delta G^*$  (corresponding to  $r^*$ ) is thus maximum free energy requirement occurs at the radius  $\mathfrak{r}^*$ , and since the free energy corresponds to the cluster size at which the surface and bulk terms exactly bulance – it The point at which the curve crosses the x axis, which occurs at  $t = 1.5t^*$ the stability of the mother phase (supersaturated vupour in this case) is threatened. formed by fluctuations (whose probability decreases in proportion to exp ( $-\Delta G/kT$ )) bottleneck' to the formation of the new phase. Once such a critical jucteus has been the maximum free energy barrier in the nucleation process, and constitutes the kinetic decreases in both directions away from this maximum, the drop will either grow or through a maximum with increasing size of the cluster. The size corresponding to this Figure 6.1 The overall free energy ( $\Delta G_{mad}$ ) for the formation of a cluster passes has no great significance insofar as nucleation theory is concerned

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indicated that this equation  $p_{\bullet}$  is the partial pressure of the vapour in the critical bubble, and the critical bubbl approximations are not valid, a fuller account must be taken of the parameters going to make up C. According to Döring (1937, 1938), C is given by constant for small ranges of supersaturation. In those instances where such  $\alpha = 1$ , and T. The value of C can usually be considered to be approximately which varies relatively slowly with  $\sigma$ , the supersaturation, defined as above,  $\sigma$  =

$$C = [6\gamma/\pi m(3-b)]^{1/2} \cdot \exp(-\Delta H_{\text{vap}}/kT)m_0$$
 (6.9)

since for b>3 this leads to a negative square-root term. Döring thus restricted (1 cm<sup>3</sup> in the present context). The quantity  $b = (p^* - P)/p^*$  introduces a problem. vaporization per molecule, and  $n_0$  is the number of molecules per unit volume appropriate temperature, m is the molecular mass,  $\Delta H_{
m vup}$  is the enthalpy of where y is the interfacial tension between the liquid and its vapour at the Pound (1963) who give as an alternative to eqn (6.9) for C: his equation to cuses where b < 3. This problem was surmounted by Hirth and

$$C = \Delta G^*/(3\pi k T^{*2})^{1/2} \cdot p^*/(2\pi m k T)^{1/2} \cdot 4\pi r^{*2} \cdot n_0$$
 (6.10)

egn (6.9) This can also be expressed in other terms which emphasize the similarities with

$$C = \Delta G^{*}/(3\pi kTi^{*2})^{1/2} \cdot n_{s} v \exp(-\Delta H_{vap}/kT) \cdot 4\pi i^{*2} \cdot n_{0}$$
 (6.11)

and is the vibrational frequency of the liquid molecules. where  $n_i$  is the number of molecules per square centimetre in the liquid surface

expressions (6.9), (6.10) or (6.11) for the pre-exponential, a means of evaluating  $p^{\alpha}$  is needed. Hirth and Pound (1963) showed that the transcendental eqn (6.12) provides the required expression In order to compare experimental results with eqn (6.8), together with

$$kT \ln (p/p^*) = O(p^* - P)$$
 (6.12)

# Homogeneous nucleation, two-component system

second component is a dissolved gas. With small modification, the equations developed above are used again. There are two main modifications required to Let us now briefly consider the case of a two-component system, where the surface tension by the dissolved gas. the theory, these being that the effective pressure in the critical bubble nucleus is increased by the presence of the dissolved gas, and the modification of the

Firstly, the pressure inside the bubble  $p^*$  is now composed of the sum of the

the liquid p, together with the partial pressure of the

(6.13) (

concentration of dissolved but, and the isthe corresponding concentrationtover a flat surface at the applied pressure P, then the property of the policy of the pressure P, then the policy of the pol The same authors showed that  $p_v = \varphi p_{vap}$ , where  $\varphi$  is given by

$$= \exp \left[ O(P - P_{\text{vap}})/kT - c_2/c_1 \right]$$
 (6.15)

nucleation equation reads in moles per unit volume (ca. 55.5 M for water). With these modifications, the here O is the molecular volume of the solvent and  $c_1$  is the solvent concentration

$$J = C' \exp \left[ -16\pi \gamma^3 / 3kT (Pc_2/c_{2e} + \varphi P_{WP} - P)^2 \right]$$
 (6.16)

solvent, a factor B (=1 in the present discussion), the surface tension  $\gamma$ , and the constant (as before), but includes N, the number of molecules per unit volume of where use has been made of eqns (6.14) and (6.15). Now, C' is not strictly a supersaturations, where  $\varphi p_{vup} << P c_2 l c_{2e}$ , then the bracketed denominator in eqn al. (1970, 1986) for details. Lubetkin and Blackwell (1988) showed that at low molecular mass of the gas species in. The interested reader is referred to Ward et (6.16) simplifies to give

$$= C' \exp \left[ -16\pi \gamma^3 / 3kT (\sigma^P)^2 \right]$$
 (6.17)

where  $\sigma$  is the saturation ratio,  $\alpha = c_2/c_{2e}$  (see eqns (6.7) and (6.16)), minus one; thus  $\sigma = \alpha - 1$ . Equation (6.17) is now in a form to be directly compared with experimental data.

alter the interfacial tension. Since this quantity, y, appears to the third power in the exponential, it will exercise a considerable influence on the rate of nucleation This question is addressed in detail in Section 6.4. Secondly, the adsorption of the dissolved second component will in general

Heterogeneous nucleation, single-component system

Bubbles formed at a surface (e.g. the walls of the container, specks of dust or other inhomogeneities), rather than in the bulk of the solution, are said to be degree to which it is easier varies according to two main parameters: (i) the easier (i.e. occurs at lower values of  $\sigma$ ) than for the homogeneous case. nucleated 'heterogeneously'. Usually, heterogeneous nucleation of bubbles contact angle  $\theta$  of the gas/solution/solid interface; and (ii) the geometry z.

### The contact angle 8

As the contact angle increases away from zero (where nucleation is exactly difficult as for the homogeneous case), it becomes easier for bubbles to

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expressed appearatice of a factor finitional the componential enthances of the componential enth formed Mathematically, this increased ease of formation is expressed by the मार्गिस् ६ अध्या भी महार ग्रह्मात्री मुन्दी अल्ला-इस्टीज स्वाङ्गातालामी सन्दर्भा

(1) The least the content of the second of describinges in the pre-exponential are usually negligible in their effect on I when @ .compared with changes in the exponential term, and this is the justification for treating the pre-exponential as a constant.

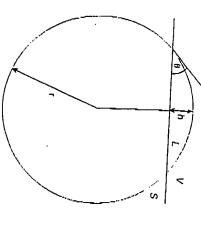
Thus f(0) is given by

$$f(\theta) = [2 + 3 \cos(\theta) - \cos^{3}(\theta)]/4$$

(6.19)

changes from a size as large as that for the homogeneous case when  $\theta=0^{\circ}$  to zero 180° and, correspondingly, the free energy barrier to the formation of bubbles This function changes from 1 when  $\theta=0^\circ$  (i.e. 'perfect wetting') to 0 when  $\theta$ 

is governed by the contact angle, as shown in Figure (6.2). zero, so the critical bubble will adopt the shape of a spherical cap, whose volume needed for nucleation is to note that, as the contact angle increases away from Conceptually, the easiest way to understand this reduction in free energy



opposite of the case for bubbles, where the function  $f(\theta)$  goes from 0 to  $\theta=180^\circ$  (i.e. non-welling), to 1 for  $\theta = 0^{\circ}$  (i.e. perfect welling), as expressed by eqn (6.19) the volume of the whole sphere, of radius v. The function  $f(\theta)$  goes from 1 for  $\theta=$ 180° (i.e. non-wetting), to zero for  $\theta=0^\circ$  (i.e. perfect wetting). Note that this is the volume of the cap gives the function  $f'(\theta) \cdot V = [2-3\cos(\theta) + \cos^3(\theta)]V/4$ , where V is sphere radius r and the contact angle heta. Eliminating h from the expression for the forming on a solid surface. The maximum height of the cap h is a function of the Figure 6.2 The spherical cap model of a nucleus of a partially wetting liquid

The geometry of the nugleation site.

gilligited and counted depressions well-defined geolinetries (e.g. spherical and control depressions and The Administration of the Partie in the Partie in the Partie in the Administration of the Partie in the Partie in

Heterogeneous nucleation, two-component system

 $\theta$  and in the geometry of the nucleation site for the case of heterogeneous nucleation in two-component systems. Essentially, it is found that nucleation and the conical pit together, the factor can be called  $f(\theta,\beta)$ , and is defined as into the pre-exponential term, which we are ignoring in the present analysis) which reduces the barrier to nucleation. If we take the effect of the contact angle conical pit of half-angle \( \beta \), introduces a factor in the exponential term (and also becomes considerably easier in certain cases, and in particular for conical pits. A Equation (6.17) can be modified to take account of variations in the contact angle

$$f(\theta, \beta) = [2 - 2\sin(\theta - \beta) + \cos(\theta)\cos^2(\theta - \beta)/\sin(\beta)]/4$$
 (6.20)

and the modified nucleation equation becomes

$$J = C''' \exp \left[ -16\pi \gamma^3 f(\theta, \beta) / 3kT(\sigma P)^2 \right]$$
 (6.2)

to below (Section 6.4). of the analysis above has been criticized (Lubetkin, 1989a, b), and this is referred or  $\beta$  result in such large (negative) values of the exponential term in eqn (6.21) reasonable rates of nucleation at low supersaturations. Small changes in either B numerical value (ca. 10-5), and it is chiefly this which results in predictions of of half-angle of about 5°, with contact angles of about 90° (Wilt, 1986). The system, supersaturations of around 4 are sufficient to cause nucleation in cavities that it becomes impossible to evaluate the full expression for J. The whole basis (Carr, 1993). The factor  $f(\theta,\beta)$  used by Wilt is chosen to give a very small factor  $f(\theta,\beta)$  becomes negative when  $\theta-\beta>90^\circ$ , and the treatment breaks down saturation easily attainable in practice. As a concrete example, for the CO<sub>2</sub>/water predicts reasonable rates of formation of bubbles under conditions of With these modifications, and for some values of  $\gamma$ ,  $\theta$ ,  $\beta$  and  $\sigma$ , eqn (6.21) super-

Single-component nucleation experiments - boiling

and Foust (1955), while Clark et al. (1959) used macroscopically polished theoretically expected. Deliberately roughened surfaces were employed by Corty experiments all share the feature that the superheat limits are not as large as contact angle) were promoting nucleation or bubble formation. These early generally heterogeneous nucleations sites of unknown detailed geometry and tion for such apparent experimental failures is that Harvey nuclei (and more gave sometimes confusing and irreproducible results. The most likely explana-Wismer, 1922) attempting to measure superheat limits on bulk samples of liquids reader is referred to Cole's (1974) review. Briefly, early experiments (see e.g. This field is really too large for a satisfactory treatment here, and the interested

for their high speed photographic investigations, identified

att 1971) The results of these experiments appear to agree much more closely southens with experiments. (see also Skripo vand Ermakov, 1964; Sinitsyn and Skripov, 1968; Blandeller (11)

with expectations of the literal conditions for the source states and the source states and the source states and the source states are states as the source states are source states and the source states are source states and the source states are source states are source states and the source states are source states and the source states are source states o-component nucleation experiments

it is hydrophilic or hydrophobic, has important consequences. This is discussed shows that the nature of the hetero surface, and in particular the degree to which attempted to compare the results with the classical heterogeneous nucleation rate of nucleation of bubbles of CO2 from supersaturated water solutions, and Blackwell (1988), and Lubetkin (1989a, b) have reported measurements on the carbonated drinks (see e.g. Findlay and King, 1913). More recently, Lubetkin and substantial qualitative and semiquantitative literature on the gas content of other than electrochemically evolved gases) are rare, although there is a more fully in Section 6.4. theory of Wilt (1986) with rather variable results. The interpretation of the data teports of experiments on bubble nucleation in supersuturated gas solutions

or by acoustic means, where rarefaction waves similarly introduce negative Cavitation is the process of bubble formation by reduction in pressure. supercritical size of the cavity nucleus is not (as might be supposed) the transfer reduction may be effected by mechanical means, placing the liquid under tension pressures. It is of interest to note that the elementary step in the growth to on liquid to growing cavity (Hirth and Pound, 1963). filiquid molecules to the vapour in the cavity, but the transport of vacancies

provide supercritical nuclei, and the further growth of these nuclei would then be insufficiently so to give spontaneous nucleation, cavitation could potentially of the cavities which liberates enough mechanical energy to cause the damage obvious drive for further growth - indeed, it is often the extremely rapid collapse expected in the case of cavitation produced by acoustic means) there is no have been studied, and will not be further addressed here, except to note that if outpace incipient bubble collapse. found on ships' screws. Clearly, in a solution that is supersaturated, but the bubble has been produced by a transitory change in pressure (as might be The question of the further growth of the bubbles once formed uppears not to assuming that transport of the growth units was adequately ᡖ

and the liquid, the observed rupture could be related to a calculated tension sealing and then cooling them; from the known thermal expansivities of the glass The earliest attempts were made by completely filling glass tubes with liquids. Cavination experiments have been conducted using a variety of techniques.

> pressures by bellows (Vincent, 1941) (Meyer, 1911; see also Kenrick et al., 1924). The direct application of negative usion that cavitation (in con 1741, 1943) and centrifugal r. 01295 m. b. 1953 m. c. c. direct app with many other nucleation methods have been

Table 6.1 Calculated and experimental strengths of various liquids"

pecial precautions are taken.

Liquid	Theoretical fracture pressure (atnios)	Obxerved fracture pressure (atmos)
Water	-1380	-270
Chloroform	-318	-290
Benzene	-352	-150
Acetic acid	-325	-288
Aniliae	-625	-280
Curbon tetrachloride	-315	-275
Mercury	-23100	-425

Courtesy of Hirth and Pound (1963)

# Electrolytic and chemical bubble generation

## Electrolytic bubble generation

of heterogeneous nucleation. between the hetero surface and the growing nucleus/bubble not met in other cases electrochemical conditions are altered. This introduces a variable interaction will carry a charge, the sign and magnitude of which will vary as the however, that bubbles will in general be charged, and the electrode surface itself and growth on surfaces other than those of electrodes. It should be remarked electrolytic bubble generation is not markedly different from heteronucleation published; for a recent example, see Sides (1986). However, in general terms, This is a wide topic and really deserves a review in itself, and muny have been

strongly influenced by subtle changes in composition of the electrode surface, expected that the size of the bubbles upon detachment from the electrode will be kinetics (by altering diffusion rates, for example). in the electrochemical potentials of the various species and phases) and the and by the electrostatic interaction. Some of these issues have been addressed in the literature (Brandon and Kelsall, 1985; Brandon et. al., 1985). This specific interaction will alter both the thermodynamics (through changes Furthermore, it is to 헍

The chief advantage of using an electrolytic method for nucleation and growth

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ould be one of the three, imosi extensively studied species; the others being was a limited species.

Recently, a new technique has become available which shows considerable hus been used to differentiate between the importance of mass transport and subsequent growth of bubbles (Carr et al., 1989), and the subsequent report of Cabrielli et al. (1991) confirmed the promise of this novel method. instantaneous effect on the apparent attached mass. The first report of this method shows that information may be obtained both on the nucleation and the molecular layers of adsorbed species. A bubble arising at such a surface has an square centimetre) and has been shown to be capable of detecting monuhas great sensitivity to changes in attached mass (of the order of nanograms per pronsise in this regard. The electrochemical quartz crystal microbalance (EQCM) diffusion, but these experiments lack in either temporal or spatial resolution obtained from the transient current behaviour, particularly on microelectrodes While studies of the growth kinetics of electrogenerated inmon (see e.g. Glas and Westwater, 1964; Verhaart et al., 1980); few appear have been undertaken on bubble nucleation kinetics. Indirect evidence rogen and oxygen. bubbles are relatively THE SECTION A 6576 ANY

## Chemical bubble generation

and current practice uses curbonates, nitrates, hydrogen peroxide, and diazo produce the foam. Careful control of the initial particle size of the chosen the carbon dioxide gas released in the reaction of the isocyanates may be used to other chemically induced gas releasing processes. In urethane foam production, decomposition reactions producing guses are the most obvious type to exploit, reaction which does not involve the passage of an electric current. Thermal The supersaturated gas/liquid solution can of course be produced by a chemical milling to the appropriate size. but the thermal instability of many of the obvious candidate reactants may inhibit reactant(s) provides the possibility of complete control of the final bubble size derivatives. Thermal decomposition can be replaced by acid-base reaction, or

### Harvey nuclei

existing bubbles whose size is sufficiently small to prevent creaming under subsequent sections, we consider three such sources: Harvey nuclei and prenucleation step, if there are pre-existing sources of bubbles. Here and in the simply a matter of where the pre-existing bubble is located (although for Harvey The formation of macroscopic bubbles may take place without the need for a nuclei this must be at a solid-liquid interface, by definition (Harvey et al., gravity, and entrained or sparged bubbles. The distinction between these is not 1944a, b, 1945, 1947; see also Bankoff, 1958), but includes possible differences

> in size of the bubble source. In the case of Harvey nuclei, the source is any I usually) re-entrant cavity of such geometry and size that the entrapped gas ble for displacement by the suirounding liquid phase. The size requirement is disease after more detail below that in all exerts base to be linger than the following the suirounding the size of the such that the suirounding that that the suirou

will usually have previously been in contact with air; and air-filled cavities will as many Harvey nuclei as possible. granules during distillation, where the deliberate (if unstated) aim is to introduce system. Perhaps the most familiar everyday example is the use of antibumping potentially serve as Harvey fuclei for the formation of bubbles in the of significance, since any container or indeed adventitious solid particl

experimentally by Griffith and Wallis (1960). In the case of bubble formation behaviour of sites of known geometry during boiling of water were tested the stability of Harvey nuclei have been studied by Cole (1974), while the by Lubetkin (1989b). trom a supersaturated gas solution, similarly well-defined sites were examined The thermodynamic and to a lesser degree the hydrodynamic requirements for

### Pre-existing bubbles

contain bubbles. Naturally, because of the generally large density difference Most liquids which have been subject to shaking or stirring in a container will as the ratio of the gravitational force to the Brownian force on the bubble: importance of creaming will be regulated by the Peclet number, which is defined determined by bubble diameter. For a given liquid/vapour combination, the between liquids and vapours or gases, creaming will take place on a time-scale

$$P_{c} = \Delta \rho v r / kT \tag{6.22}$$

where  $\Delta p$  is the density difference between liquid and bubble,  $\nu$  is the bubble short time-scales, and as they become smaller still, they will effectively not Creaming will only be important where  $P_e >> 1$ , which for water at room volume, r its radius, k is the Boltzmann constant, and T the absolute temperature. cream at all. Such behaviour is well known for colloidal dispersions of solids and Obviously, bubbles much smaller than this size will not cream on reasonably temperature will be satisfied for bubbles of rather more than  $1\,\mu m$  in diameter. respects, and so it is here; bubbles are as subject to dissolution and coalescence as are liquid droplets or solid particles. These issues are addressed in Section 6.4. collision, and hence coalescence, is less important. For the case of supersaturated concentrated than other conventional colloidal systems, so that Brownian Stability against creaming or sedimentation is no guarantee of stability in other needs re-emphasis here. The issue is not settled by such an analysis, however. liquids, and the potential long-term (kinetic) stability of such suspensions hardly gas solutions at least, there is no problem of dissolution for supercritical-sized For the present, suffice it to say that bubble suspensions are frequently less stabilising bubbles than in other colloidal systems, and this aspect is dealt with bubbles. Furthermore, surfactants may play an even more important role in more fully in Section 6.5.

In the cuse of aqueous media, it is known that bubbles may be very persistent

The bubbles considered by D.A. nigo are generally much larger than this non-creaming size (say between about 30–100 µm in diameter), and his chief interest the serwill satisfy the Peclet criterion, and be kinetically stable over long periods. contain a Jurge number of bubbles and that stutistically, approportion of

surge of bubbles, as the pre-existing, submicroscopic bubbles rapidly grew to a account, and by whether the rate of bubble appearance dropped with time more of whether the imposed change was sufficient to cause nucleation on its own needed, and none night have taken place; this could only be decided on the basis nucleation, but such an impression might be false: no nucleation would be visible (or detectable) size. The appearance would be of a rapid burst of (reduction of pressure, increase in temperature etc.) would then give rise to a rapidly than the rate of relief of supersaturation apparently warranted s in the stability of such relatively large bubbles against dissolution. sudden change in conditions in such a stable bubble-containing system

the related question of how to get rid of the bubbles; the application of a pre-existing bubbles last? Unfortunately, there seems to be no clear answer to this of the pressure required will of course depend on the size of the bubble to be sufficiently great pressure will collapse all bubbles in the system, the magnitude question at present. By analogy with colloidal suspensions of solids or liquids, nearly 150 years after their preparation. It is relatively easy to give an answer to Faraday's original gold sols are still stable at the Royal Institution in London. however, we may speculate that the life-times may be very long indeed a fresh crop of microbubbles reduction of the applied pressure, that the released gas will again nucleate to form in excess of 1000 atmos. Worse still, there is always the prospect that upon removed. Rather more discouragingly, these pressures are often very large, and From a practical standpoint, the interesting question is how long might such

# 6.2.2 Non-spontaneous bubble formation

a liquid by pumping gas (usually through a frit, filter or bubble column) into the and shape of a bubble forming at an orifice are identical (with an appropriate sign the subject of an extensive literature. We note that the mathematics of the size understood. The thermodynamic factors ruling bubble production at an orifice are of producing monosized bubbles, and furthermore the theory is reasonably well bulk liquid. In principle, this should be the most controllable and reliable method The term 'sparging' is intended to cover the insertion of gas bubbles directly into

> in this area abound (a useful book in this context is that by Harrland and Harrley, reversal) to the treatment of a liquid drop similarly formed. Reviews and books

the bubbl readily be calculated from the force balance about any horizontal uguonal

$$(6.23)$$

any point is given by g is the acceleration due to gravity. The pressure drop  $\Delta p$  across the interface at where x is the horizontal distance to the bubble axis at an angle of to that axis V is the bubble volume,  $\Delta p$  is the density difference between gas and liquid, and

$$\Delta p = 2\gamma lb + g\Delta \rho z \tag{6.24}$$

and  $R_2$  to the difference in pressure  $\Delta p$  across the curved interface and to the Making use of the Laplace equation relating the principal radii of curvature R. interfacial tension y.

$$\Delta p = \gamma (1/R_1 + 1/R_2) \tag{6.25}$$

gives

$$\gamma(1/R_1 + 1/R_2) = 2\gamma/b + g\Delta\rho z$$
 (6.26)

to the bubble shape, and given by This equation can be written in dimensionless form using a parameter \( \beta\_i \) related

$$\beta = \Delta \rho g b^2 / \gamma \tag{6.27}$$

b is the radius of curvature at the apex of the bubble. Combining these parameters into a single equation gives

$$[1/(R_1)/b] + [\sin(\phi)/(x/b)] = \beta(z/b) + 2$$
 (6.28)

and defining a new quantity H given by the apex. The ratio  $d_s/d_t$  is often called S, which is experimentally determined diameter at the equator of the bubble and  $d_s$  is the diameter at a distance  $d_e$  from terms of two characteristic diameters of the bubble  $d_{\mathbf{e}}$  and  $d_{\mathbf{s}_1}$  where  $d_{\mathbf{r}}$  is the Adams (1883). More conveniently, the required quantities can be expressed in This is the form of equation solved numerically (by hand) by Bashforth and

$$H = \beta (d_{\nu}b)^2 \tag{6.29}$$

it follows that

$$\gamma = g\Delta \rho d_e^2 / H \tag{6.30}$$

available. Knowing (experimentally) the value of S, Equation (6.30) is exact, and tabulated values of S as a function of I/H are readily appropriate value of  $H_i$  and thus from eqn (6.30)  $\gamma$  can be determined. This is the tables give the

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single bubble regime, the intermediate regime, and the jet regime. The single al., 1984), little is known theoretically. Three regimes can be distinguished: the more difficult problem, and while empirical correlations are available (Perry et bubble regime can be reasonably satisfactorily described by the thermodynamic to be accounted for, since rapid bubble formation is usual in sparging. This is again to the the detachment volume. Usually, the dynamics of the fluid fluid interface have the analyses presented above. It is simple to show that the frequency,  $\tilde{\omega}_i$  of bubble in a liquid/gas combination characterized by densities  $\rho_1$  and  $\rho_g$ , respectively, is detachment for a volumetric flow rate of gas of arrho, and an orifice diameter of Dof sparging equilibrium calculations are intidequate to predict THE PROPERTY OF THE PARTY OF TH

$$\bar{\omega} = Qg(p_1 - p_g)/\pi D\gamma$$

orifice. Despite their name, these 'jets' actually consist of many small bubbles predicted by eqn (6.31), and the bubbles themselves tend to increase in size. The 200-2100, the frequency of bubble detachment increases more slowly than theoretical description of this regime, and even empirical correlations are not (typically between about 200 \u2224m and 4 mm in diameter). There is no adequate jet reginte is characterized by turbulence, and the appearance of 'jets' from the In the intermediate regime, represented by Reynolds numbers of about

### Entrainment

Entrainment covers those situations where gas is enveloped by the liquid at the control of the bubble size difficult, and for this reason this method of bubble Clearly, in such circumstances, the violence of the motion involved makes fountains or by wave action or other turbulent motion in oceans, rivers and lakes. violent motion. Common examples are the entrainment of air into water in interface between the two phases, and most usually occurs where the liquid is in successfully entrain large quantities of air. An approximate expression for of liquid is directed at an appropriate velocity into a pool of the liquid, can formation will not be considered in detail here. Cascade systems, where the jet volumetric ratio of gas to liquid  $Q_{\rm g}/Q_{
m l}$  thus entrained is given by

$$Q_{g}IQ_{1} = 0.0316(V^{2}p_{1}LI\gamma_{8})^{1/2}$$

(6.32)

where V is the jet velocity,  $\rho_1$  is the liquid density,  $\gamma$  is the surface tension, and is the length of the jet.

chief means of introducing bubbles into fluid systems. Mechanical agitators may Agitational methods are common in industrial practice, and are one of the

> work by a combined mechanism involving both entrainment and attrition (see le-size produced by a mechanical agitutor is

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The same mechanical/hydrodynamic processes for apply the factors discussed below but, assuming a sufficiently long survival, these eya the responsible for the formation of the original, larger bubbles, and break up is entrapment of gas Of course, the lifetime of bubbles so formed will depend on and there is a substantial, if mainly empirical, chemical engineering literature likely to follow. These processes, which we refer to as 'attrition', are complex available (Perry et al., 1984). To the second second

used a rotating wire cage to measure foun volumes as a function of the tip speed of the cage, at various surfactant concentrations. In all cases, the foam volume reviewed by Tadros and Vincent (1983) and by Walstra (1983). similar phenomenon in emulsions, a subject which has been extensively Clearly, mechanical break up of bubbles will share common features with the good reasons for believing that dilute suspensions would not behave identically behaviour would also apply to more dilute bubble suspensions, although there are the agitation caused foam breakage. It is likely that, in a general way, this sort of concentration. This velocity was identified with the critical value, beyond which plots showed very sharp maxima at a velocity which increased with the surfactant An elegant and revealing experiment was performed by Prins (1976), who

### တ ယ Growth of bubbles

grow; growth will be fostered by the same conditions of supersaturation that gave Whatever the means by which a supercritical bubble is formed, it will tend to greater than unity, bouyancy would result in subsequent growth. noted above, such conditions may be found in acoustic cavitation). Even then if rise to the nucleation event. Only in the case of a nucleation pulse, rapidly the cavity formed was sufficiently large that its Peclet number was substantially followed by a return to equilibrium, would further growth not take place (as

separately, even though they clearly have many attributes in common It is convenient to consider bubble growth at a surface and free bubble growth

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# 6.3.1 Bubble growth at a surface

and pressure, followed by growth essentially dominated by diffusion, either of be distinguished during the growth. Firstly, there is a short period, typically about and from the heating engineering literature. Broadly speaking, two regimes can from the electrochemical literature (see e.g. Westerheide and Westwater, 1961) The primary sources for information on the growth of bubbles at surfaces are 10 ms, where the growth is controlled by surface tension forces, inertia, viscosity